The Astrophysical Journal, 661: L97–L100, 2007 May 20

A SEARCH FOR VARIATION IN THE H_2O ORTHO-PARA RATIO AND ROTATIONAL TEMPERATURE IN THE INNER COMA OF COMET C/2004 Q2 (MACHHOLZ)

Boncho P. Bonev,[1,2] Michael J. Mumma,[2] Geronimo L. Villanueva,[2,3] Michael A. Disanti,[2]
Richard S. Ellis,[4] Karen Magee-Sauer,[5] and Neil Dello Russo[6]

Received 2007 January 5; accepted 2007 March 26; published 2007 April 24

ABSTRACT

We present spatially resolved measurements of the rotational temperature and ortho-para ratio for H_2O in the inner coma of the Oort Cloud comet C/2004 Q2 (Machholz). Our results are based on direct simultaneous detections of ortho-H_2O and para-H_2O via "hot-band" fluorescence near 2.9 μm. We find a well-defined decline in rotational temperature with increasing nucleocentric distance (up to ~1000 km). The ortho-para ratio remains constant (within stochastic uncertainty) with increasing nucleocentric distance and is close to the statistical equilibrium value of 3.0 (2.86 ± 0.06 [0.17], including, respectively, stochastic [systematic] uncertainty), resulting in spin temperature $T_{spin} \geq 34$ K. We compare the present results with those reported for other comets and discuss the difficulties in interpreting spin temperatures deduced from measured ortho-para ratios. Improved understanding of the special conditions that enable nuclear spin conversion would test the extent to which derived spin temperatures reflect the formative history or the processing record of cometary ices.

Subject headings: comets: general — comets: individual (C/2004 Q2 (Machholz)) — infrared: solar system

Online material: color figure

1. THE TWO NUCLEAR SPIN SPECIES OF H_2O AND THE PUZZLE IN UNDERSTANDING ORTHO-PARA CONVERSION

Molecules containing identical nuclei display isomers grouped according to their total nuclear spin. The probability for conversion between different isomers is under many circumstances low, but not zero. However, the conditions that assist this process are often not well defined, and an improved understanding could elevate spin conversion to an important tool in science (Hougen & Oka 2005; Chapovsky & Hermans 1999).

The H_2O molecule is organized into two isomers depending on whether the nuclear spins of its H atoms are parallel (ortho "ladder") or antiparallel (para "ladder"). Radiative and collisional transitions between ortho and para states are strongly forbidden. Recent studies suggest that the radiative nuclear spin conversion times of H_2O are more analogous to the extremely long conversion times of H_2 than those of species like CH_4 for which faster conversion can occur (Miani & Tennyson 2004).

Nuclear spin "flip" can be accomplished via bond splitting and reformation with other H atoms. Another possibility is that of dipolar magnetic spin conversion on ice surfaces (Limbach et al. 2006). Notably, Limbach et al. predict the ortho-para ratio (OPR) to change in an isolated hydrophilic surface, implying that the OPR measured in H_2O gas released from a cold ice surface would reflect the surface temperature. This conclusion adds to the "physicochemical puzzle" in understanding the conditions for ortho-para conversion. But (if proven definitively) it might have implications outside the chemical laboratory. OPRs in cometary H_2O were first measured in 1P/Halley (Mumma et al. 1987, 1988 [revised retrieval]), and the low values found suggested that information from the formative stage of our planetary system had been preserved. Measurements on subsequent comets (§ 2) have re-energized interest in nuclear spin conversion.

2. H_2O SPIN TEMPERATURES IN COMETS

The lowest energy level of para-H_2O lies 23.8 cm^{-1} (~34 K) below the lowest ortho level, so the ratio between the total populations of ortho and para states is temperature-dependent (curve in Fig. 1, based on Mumma et al. 1987). The *x*-axis (Fig. 1) represents the spin temperature (T_{spin}), defined as the temperature that would correspond to a given OPR if in local thermodynamic equilibrium. OPRs are extracted from comeasured emission lines of ortho-H_2O and para-H_2O, and spin temperatures are inferred by placing the measured OPR on the theoretical curve in Figure 1. The OPR error limits then define the corresponding uncertainties in T_{spin}. For example, $T_{spin} = 21 \pm 2$ K for point 7b in Figure 1, while $T_{spin} > 29$ K (1 σ lower bound) for point 6. Note that the relation between OPR and T_{spin} is nonlinear. In the asymptotic limit (OPR = 3.0, the statistical equilibrium value), the spin temperature (or its 1 σ upper bound as in the case of points 2, 5, 6, and 9 in Fig. 1) is not constrained by the OPR measurement. OPRs in some comets fall below the statistical equilibrium value, while OPRs in other comets are consistent with it within uncertainties of 1–3 σ. Derivations for T_{spin} for CH_4 and NH_3 (based on NH_2 emission) have also been published (see Kawakita et al. 2006, 2005).

The meaning of these spin temperatures has interested astronomers since H_2O was first detected in the atmosphere of a comet in the mid-1980s. Crovisier (1984) and Mumma et al. (1987, 1988, 1993) explored the idea that T_{spin} is a faithful measure of the chemical formation temperature of cometary H_2O. To date, there is no definitive evidence that H_2O molecules undergo nuclear spin conversion during their long residence in the interior of a comet or after sublimation in the coma. However, the meaning of spin temperatures in comets is "enig-

[1] Department of Physics, The Catholic University of America, Washington, DC 20064; bbonev@ssedmail.gsfc.nasa.gov. Work was begun while a graduate student at the University of Toledo, Toledo, OH 43606.
[2] Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, MD 20771.
[3] NASA Postdoctoral Fellow.
[4] Department of Astronomy, California Institute of Technology, Pasadena, CA 91125.
[5] Department of Physics and Astronomy, Rowan University, Glassboro, NJ 08028-1701.
[6] Space Department, Planetary Exploration Group, Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20023-6099.

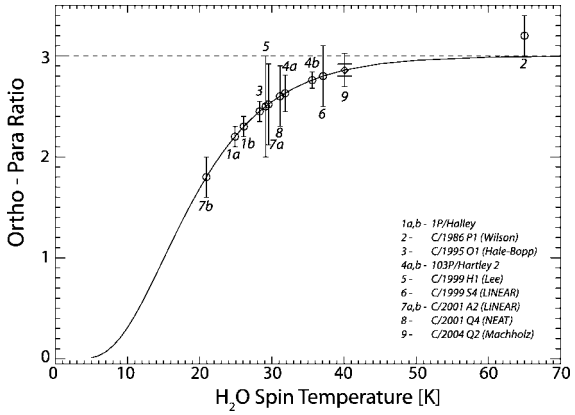

FIG. 1.—Ortho-para ratios for H_2O in comets. Individual OPR measurements are originally reported in Mumma et al. (1988: 1a, 1b, and 2); Crovisier et al. (1997: 3, 1999: 4a, b); Dello Russo et al. (2005: 5, 6, 7a, and 7b); Kawakita et al. (2006: 8). The weighted mean for this Letter (9) is also shown (*diamond*). In addition to its overall uncertainty, the uncertainty accounting for photon noise alone (*smaller error bar*) is also indicated (see discussion in § 4). The curve is based on Mumma et al. (1987). The OPR measurements are placed on the curve to identify the corresponding spin temperature, while the OPR measurement uncertainty defines the error in $T_{\rm spin}$. The OPR value corresponding to statistical equilibrium is indicated as a dashed horizontal line.

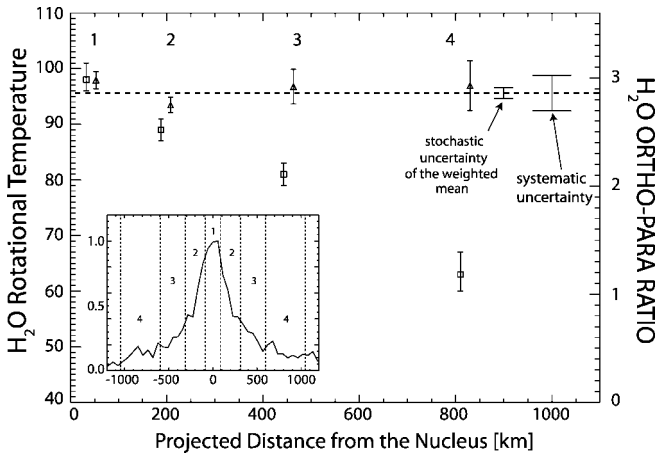

FIG. 2.—Rotational temperatures (*squares*) and OPRs (*triangles*) measured for H_2O in the inner coma of C/2004 Q2 (Machholz). The weighted mean OPR value is indicated by the dashed horizontal line (see text for discussion of stochastic and systematic uncertainties). *Inset*: Spatial profile (normalized intensity vs. projected nucleocentric distance) of H_2O emission in C/2004 Q2. We summed (column by column) the signal of all detected water lines to form a spatial profile with high signal-to-noise ratio (see Bonev et al. 2006). The slit was oriented approximately south-north on the sky, with the projected sunward direction perpendicular to it. Each temperature and OPR measurement corresponds to a range of cometocentric distances, as indicated.

matic," considering the "gaps" in our understanding of the conditions permitting nuclear spin conversion. Improved understanding would benefit from development of reliable laboratory techniques for separation and enrichment of a particular isomer (see Ustynyuk et al. 2006; Sun et al. 2005; Tikhonov & Volkov 2002) and also from the realization of IR spectrometers with adequate sensitivity for testing the extremely weak ortho-para radiative transitions predicted by Miani & Tennyson (2004). In parallel with these efforts we need to better understand and ultimately improve the reliability of $T_{\rm spin}$ measurements in comets. Our purpose is to conduct multiple independent measurements in the coma within a single observation. To that end, we present spatially resolved OPR retrievals in the coma of comet C/2004 Q2 (Machholz).

3. SPATIALLY RESOLVED ROTATIONAL TEMPERATURE AND ORTHO-PARA RATIO MEASUREMENT IN A BRIGHT OORT CLOUD COMET

The Oort Cloud comet C/2004 Q2 (Machholz) was observed on UT 2005 January 19 (R_h = 1.208 AU, Δ = 0.394 AU) with the Near Infrared Echelle Spectrograph (McLean et al. 1998) at the Keck 2 telescope atop Mauna Kea, Hawaii. A detailed description of these observations and our methodology for spectral extraction is presented in Bonev et al. (2006). These data comprise our highest signal-to-noise ratio Keck 2 spectral library for any comet to date. The spectral region near 2.9 μm contains multiple lines of H_2O in "hot-band" fluorescence and has been explored recently in detail (Dello Russo et al. 2004, 2005). These lines have proven especially suitable for measurements of H_2O rotational temperature and OPR from ground-based observations.[7]

Figure 2 (*inset*) shows the spatial distribution of H_2O emission intensity. We extracted H_2O spectra independently for four projected (on the sky plane) distances from the nucleus, as indicated in this figure.Figure 3 shows these spectra ($\lambda/\delta\lambda \sim$ 25,000 using a 3 pixel [0.43″] slit), corresponding to regions 1–4 designated on the spatial distribution plot. To achieve adequate signal-to-noise ratio for the off-nucleus extracts (2, 3, and 4), the signal from corresponding distance from either sides of the nucleus has been combined.

The relative intensities among lines of a given isomer (ortho or para) depend on the rotational temperature ($T_{\rm rot}$) for water, defined as the Boltzmann temperature that best matches the rotational distribution within the ground vibrational state of H_2O. The relative intensities of lines from different spin isomers then provide a measure of the OPR. The methodology for retrieving these parameters from ground-based observations has been described in Dello Russo et al. (2004, 2005) and Bonev (2005). The rotational temperature is determined via *correlation* and *excitation analyses*. DiSanti et al. (2006) and Bonev (2005) show how both methods complement each other. The former method identifies $T_{\rm rot}$ for which a fluorescence model best fits the measured spectrum. The latter method finds the temperature for which the ratio between observed line flux and predicted fluorescence efficiency ($g_{\rm H_2O}$ [$T_{\rm rot}$]) is independent of rotational excitation energy. Both methods gave highly consistent results.

The rotational temperature for H_2O can be reliably determined from the relative intensities of the ortho lines alone, since they sample states whose internal rotational energies span a sufficiently broad range to constrain the distribution. We find a monotonic decrease in $T_{\rm rot}$ with increasing nucleocentric distance (Fig. 2).[8] The measured para lines encompass a much narrower range of rotational excitation and therefore cannot constrain $T_{\rm rot}$ nearly as well; thus, we assume the same $T_{\rm rot}$ for para-H_2O. However, their measured intensities agree well with those predicted using the derived $T_{\rm rot}$ (Fig. 3).

[7] In "hot-band" fluorescence, radiative vibrational excitation by solar quanta from the ground vibrational state of H_2O is followed by a cascade into intermediate vibrational levels, which are not significantly populated in the Earth atmosphere. This is the only type of emission through which cometary H_2O can be observed both directly and routinely from the ground.

[8] The distribution of $T_{\rm rot}$ in the inner coma for H_2O will be compared with that of other species in a separate paper. Note that the H_2O production rate was $\sim 2.6 \times 10^{29}$ molecules s^{-1} (Bonev 2005).

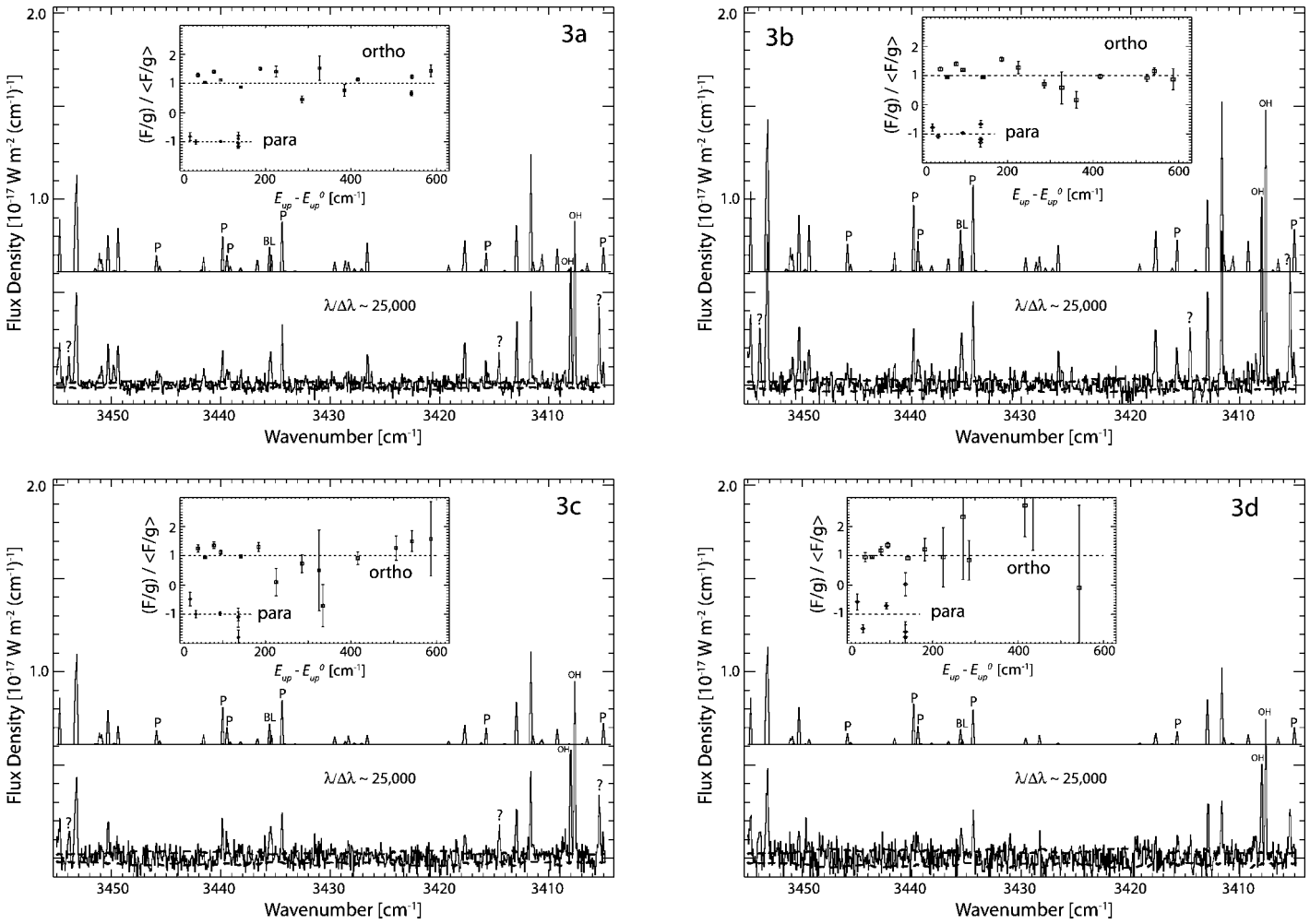

FIG. 3.—Measured (*below*) and modeled (*above*) H_2O spectra, corresponding to spatial extracts 1–4 (*panels a–d, respectively*) as in Fig. 2. The *x*-axis corresponds to the cometary rest frame. The dashed lines in the observed spectrum indicate the 1 σ photon noise envelope. In the model, para-H_2O transitions (P) and an ortho-para blend (BL) are indicated. The remaining water lines belong to ortho-H_2O. The model is calculated for the best rotational temperature and OPR for the corresponding spatial extract (Fig. 2). *Insets*: Line-by-line ratios of observed fluxes and modeled *g*-factors (F/g), normalized to their mean value ($\langle F/g \rangle$) for ortho-H_2O and for para-H_2O (the para distribution is offset for clarity). The ortho-para blend near 3436 cm^{-1} is excluded from this analysis. The spread around the weighted mean in the two distributions exceeds the stochastic uncertainties of individual points and is (presently) the limiting source of uncertainty in the OPR retrievals. The quantity on the *x*-axis is the rotational energy of the upper state for the corresponding transition. [*See the electronic edition of the Journal for a color version of this figure.*]

With $T_{\rm rot}$ determined from the emission of a single spin species, the OPR within a given aperture can be calculated from this expression:

$$\mathrm{OPR} = \frac{\langle N_{\rm o} \rangle}{\langle N_{\rm p} \rangle} = \frac{\langle F/g_{\rm H_2O} \rangle_{\rm o}}{\langle F/g_{\rm H_2O} \rangle_{\rm p}} \mathrm{OPR}_{\rm eqlb}, \qquad (1)$$

where $\langle N_{\rm o} \rangle$ ($\langle N_{\rm p} \rangle$) is the column abundance of ortho-H_2O (para-H_2O) averaged over the observed ortho (para) lines and $\langle F/g_{\rm H_2O} \rangle_{\rm o}$ ($\langle F/g_{\rm H_2O} \rangle_{\rm p}$) is the ratio of line flux to fluorescent *g*-factor averaged over the ortho (para) lines. These *g*-factors are calculated for statistical equilibrium ($\mathrm{OPR}_{\rm eqlb} = 3.0$) and are taken from the H_2O fluorescence model developed in Dello Russo et al. (2004, 2005) and Barber et al. (2006).

4. THE CONSTANT ORTHO-PARA RATIO IN THE COMA: UNCERTAINTIES AND INTERPRETATION

The retrieved ortho-para ratios are subject to both stochastic and systematic uncertainties. We show stochastic errors for each spatially resolved measurement to demonstrate that our measurements agree within the limits of photon noise (Fig. 2). A weighted mean of these retrievals results in OPR = 2.86 ± 0.06 when only stochastic errors are included. However, the overall OPR uncertainty is *not* dominated by photon noise, but by model-related uncertainties that account for the level of disagreement between the ratio of observed line flux (F) to fluorescent *g*-factor ($g_{\rm H_2O}$) as measured line by line for the ortho and (separately) for the para transitions (Fig. 3, *insets*). Our high-precision flux measurements (extracts 1 and 2) show that line-by-line deviations in $F/g_{\rm H_2O}$ correlate highly for these independently extracted spectra and therefore introduce systematic errors (i.e., they will affect OPRs retrieved from the four extracts in the same way).

This systematic uncertainty is most likely related to limitations imposed by the assumptions and accuracy of our fluorescence models. Slight inaccuracies in the *g*-factors, predicted rest frequencies, and/or corrections for telluric extinction would produce correlated (between different apertures) line-by-line scatter in $F/g_{\rm H_2O}$ as seen in the insets of Figure 3. Also, while

T_{rot} varies in the coma (Fig. 2), an "effective" value is returned for a given aperture. The scatter in line-by-line measurements might increase if the relative intensities of lines differ from those predicted using a unique T_{rot}.

The systematic uncertainty in OPR is estimated from the standard deviations of $\langle F/g_{H_2O}\rangle_o$ and $\langle F/g_{H_2O}\rangle_p$ (see eq. [1] and Fig. 2)—it clearly dominates the stochastic noise and results in a weighted mean OPR $= 2.86 \pm 0.17$. In our experience, the uncertainty of an isomeric ratio retrieved from a line-by-line analysis can underestimate the true uncertainty and result in unrealistically constrained values, if it includes only errors in photon noise but not uncertainties related to the assumptions and precision of fluorescence modeling (see also Dello Russo et al. 2006 and Bonev 2005).

For each spectral extract we verified that the retrieved OPR does not change substantially when the T_{rot} for H_2O is varied within intervals conservatively chosen to exceed the errors in T_{rot}. For example, we verified that the nucleus-centered OPR retrievals are consistent whether 108 K, 98 K (the measured value), or 90 K is adopted for T_{rot}. We also appreciate that our measurements rely on a very limited number of para lines, introducing the possibility of additional uncertainty. For that reason we verified that eliminating individual included para transitions from our analysis does not substantially alter the OPR.

Our measured OPRs are very close to statistical equilibrium (even considering stochastic uncertainty alone). Except for comet C/1986 P1 (Wilson), the T_{spin} values of H_2O, NH_3, and CH_4seem clustered near 30 K, which has raised the question of why the spin temperatures in comets (and among molecular species) are the same. However, a careful examination of the measured OPRs for H_2O and their confidence limits (Fig. 1) implies that the equilibrium value (3/1) cannot be ruled out for some of these results.

The OPR constancy (within stochastic error) in the coma confirms that pure rotational transitions[9] that convert ortho-H_2O to para-H_2O (but not the inverse) have very low probability. Our results leave the possibility for surface mediation—the OPR could have been much lower than 3.0 within the nuclear ice, but (partially) "equilibrated" on desorption from the nucleus surface whose temperature is significantly above 50 K (see § 1). Alternatively, gas phase collisions might equilibrate the spin and rotational temperatures (i.e., $T_{spin} = T_{rot}$) throughout the sampled coma. Both possibilities are inconsistent with some other comets in which T_{spin} is much less than both the rotational temperature and the (active) nucleus surface temperature. This suggests that the measured OPRs characterize the water within the nucleus of C/2004 Q2.

[9] The time required to traverse 1000 km is ~2000 s (for a [conservative] outflow velocity ~0.5 km s^{-1}). An H_2O molecule undergoes only about two dipole-allowed IR fluorescence events during this time (based on summed g-factors for the ν_1, ν_2, and ν_3 bands), so our results do not test conversion via the extremely weak, strongly forbidden vibrational transitions predicted by Miani & Tennyson (2004).

5. CONCLUSION

Improved understanding of the special conditions for nuclear spin conversion could test the extent to which spin temperatures in comets reflect the formative history of cometary ices. Although reported OPRs for some comets seem to "cluster" near $T_{spin} \approx$ 30 K, others are consistent with statistical equilibrium ($OPR_{eqlb} = 3.0$, $T_{spin} >\sim 50$ K). In C/2004 Q2 (Machholz) we find OPR $= 2.86 \pm 0.06$ (0.17), including, respectively, stochastic (systematic) uncertainty, resulting in $T_{spin} \geq 34$ K (1 σ lower bound).

The present work validates the capability for measuring spatially resolved rotational temperature and OPR retrievals from ground-based observatories, where comet studies may be conducted on a fairly regular basis. A major part of this overall objective is to build a comprehensive database for H_2O in coming years. The technique introduced in this Letter can provide critical tests of spin species conversion in the cometary coma. Finding a retrieved spin temperature that does not vary in the coma, but is significantly lower than the rotational temperature, would provide convincing evidence that the water spin temperature is not "reset" by collisions in the comet atmosphere.

We thank Jacques Crovisier for helpful comments. This work was supported by the NASA Planetary Astronomy Program under RTOP 344-32-30-07 to M. J. M. Our observations were conducted at the W. M. Keck Observatory, operated as a scientific partnership among Caltech, UCLA, and NASA. This observatory was made possible by the generous financial support of the W. M. Keck Foundation. The authors acknowledge the very significant cultural role and reverence that the summit of Mauna Kea has always had within the indigenous Hawaiian community. We are most fortunate to have the opportunity to conduct observations from this mountain.

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